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SOLUBILITY BEHAVIOR OF PURE COMPONENTS (CAMPHENE AND CARYOPHYLLENE OXIDE) AT SUBCRITICAL AND SUPERCRITICAL CONDITIONS OF CARBON DIOXIDE

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By

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Subcritical and supercritical fluids are good solvents because they possess liquid-like density and gas-like diffusivity and viscosity, which allow quick equilibration and micro pore permeation of fluid. Advantages of using subcritical and supercritical fluid are environmental friendly, less contamination of final product, energy saving and easy to control. In order to develop subcritical and supercritical processes, fundamental knowledge about thermophysical properties and phase equilibrium knowledge are crucial. With solubility data of compounds in subcritical and supercritical condition of solvent, these processes can be designed, scaled up and optimized. One major problem currently is that this fundamental knowledge is still lacking or limited to specific thermodynamic range. With all these problems, this study is significant with objectives to design and develop an experimental rig for solubility study, to investigate the effect of temperature and pressure on solubility behavior and to identify suitable mathematical model that correlates solubility data with changes of thermodynamic condition. In this study, solubility behavior of two active compounds from Malaysia local herbs, which are camphene and caryophyllene oxide, were investigated because of their medicinal values and unavailability of their solubility data. Experimental apparatus was developed based on dynamic method that coupled with off-line gravimetrically analysis for its convenience and better accuracy. As the apparatus had been assembled, it was subjected to validation with naphthalene to determine suitable flow rate for the experiment (4 ml/min) and to check the workability and accuracy of apparatus. Then, solubility study was carried out for camphene and caryophyllene oxide under subcritical (298.15 K and 303.15 K, 50 – 70 bar) and supercritical conditions (308.15 K and 313.15 K for camphene, 308.15 K and 318.15 K for caryophyllene oxide; 80 - 250 bar) of carbon dioxide. Solubility behavior of both compounds under subcritical carbon dioxide condition increased significantly with minor increment in pressure and temperature because density of solvent is very sensitive in subcritical region. In supercritical condition, retrogradation behavior happened and therefore solubility of

both compounds decreased when temperature increased. However, solubility of both compounds still increased with pressure. Three commonly used semi-empirical models, which are Bartle model, Chrastil model, and Mendez-Santiago-Teja model, were tested to correlate solubility data with density of carbon dioxide. Of these three models, Mendez-Santiago-Teja model showed excellent fitting for both compounds in subcritical and supercritical condition with average absolute relative deviation kept below 2%.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Sarjana Sains

KELAKUAN KELARUTAN SEBATIAN TULEN (CAMPHENE DAN CARYOPHYLLENE OKSIDA) DALAM KARBON DIOKSIDA HAMPIR KRITIKAL DAN LAMPAU KRITIKAL

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Bendalir hampir kritikal dan lampau kritikal merupakan pelarut yang baik kerana mereka mempunyai ketumpatan seperti cecair dan kemeresapan serta kelikatan seperti gas. Ciri-ciri seperti ini membolehkan kelarutan yang cepat dan penyerapan melalui liang mikro bendalir. Kelebihan penggunaan bendalir ini adalah mesra alam sekitar, produk akhir kurang mencemar, menjimatkan tenaga and senang untuk dikawal. Pengetahuan asas tentang termofizikal dan keseimbangan fasa adalah penting untuk membangunkan proses hampir kritikal dan lampau kritikal. Dengan data kelarutan sebatian, proses hampir kritikal dan lampau kritikal boleh direka, dinaiktaraf dan dioptimumkan. Tetapi, data kelarutan ini masih kekurangan atau dihadkan dalam syarat termodinamik tertentu. Oleh sebab ini, kajian kali ini adalah penting dengan tujuan merekabentuk satu alat kajian yang boleh mendapat data kelarutan, menyiasat kesan suhu dan tekanan pada kelarutan sebatian, dan mengenalpasti model matematik yang sesuai untuk mengaitkan data kelarutan dengan keadaan termodinamik. Dalam penyelidikan ini, kelakuan kelarutan bagi dua sebatian aktif dari herba tempatan Malaysia, iaitu *camphene* dan *caryophyllene* oksida, akan disiasat kerana ia mempunyai nilai perubatan yang tinggi dan data kelarutannya masih tidak diketahui. Alat kajian direka berasaskan kaedah dinamik dengan analisis *offline* graviti kerana cara ini senang dipasang, kurang rumit, murah dan lebih tepat. Selepas alat ini siap direka, pengesahan dengan data kelarutan naftalena dijalankan untuk menentukan kadar aliran yang sesuai bagi kajian (4 ml/min) dan memeriksa kebolehkerjaan dan ketepatan alat. Kemudian, kajian kelarutan baru dijalankan untuk *camphene* dan *caryophyllene* oksida dalam keadaan hampir kritikal (298.15 K dan 303.15 K, 50 – 70 bar) dan lampau kritikal (308.15 K dan 313.15 K bagi *camphene*, 308.15 K dan 318.15 K bagi *caryophyllene* oksida; 80 – 250 bar). Kelarutan bagi kedua-dua sebatian dalam keadaan hampir kritikal naik secara ketara dengan kenaikan tekanan dan suhu yang kecil kerana ketumpatan pelarut sangat sensitif dalam keadaan hampir kritikal. Bagi lampau kritikal, "keadaan kemunduran" berlaku dengan kelarutan kedua-dua sebatian menurun apabila suhu

dinaikkan. Walaupun begitu, kelarutan mereka masih menaik apabila tekanan dinaikkan. Tiga model semi-empirikal yang biasanya digunakan, iaitu model Bartle, model Chrastil dan model Mendez-Santiago-Teja, telah pun diaplikasikan untuk mengaitkan data kelarutan dengan ketumpatan karbon dioksida. Daripada ketiga-tiga model ini, model Mendez-Santiago-Teja paling sesuai bagi kedua-dua sebatian dalam keaadaan hampir kritikal dan lampau kritikan dengan menunjukkan purata sisihan relatif mutlak bawah 2%.

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LIST OF ABBREVIATIONS

y_2 = Solubility of solute (mole solute/mole CO_2)

$y_2^{literature}$ = Solubility data from literature (mole solute/mole CO_2)

y_2^{exp} = Solubility data from experiment (mole solute/mole CO_2)

c_2 = Solubility of solute (g/L)

T = Temperature (K)

T_c = Temperature (°C)

ρ = Density (g/L or kg/m^3)

ρ_1 = Density of solvent (g/L or kg/m^3)

ρ_{ref} = Reference density (700 g/L)

P = Presure (bar)

P_{ref} = Reference pressure (1 bar)

P_2^{sub} = Sublimation pressure of solute (bar)

a = Attraction parameter

a_{cr} = Attraction parameter at critical temperature

α = Function of reduce temperature and acentric factor

b = van der Waals covolume

c = Equation of state parameter

a_1 = Constant depending on enthalpy of solvation

b_1 = Constant depending on molar mass of solvent and solute

k = Association number of solute

R = Gas constant (J/mol K)

$\Delta_f H$ = Heat of fusion (J/mol)

T_2^m = Melting temperature of solute (K)

δ_1 = Solubility constant of supercritical fluid ($J^{1/2}\ m^{-3/2}$ or $MPa^{1/2}$)

δ_2 = Solubility constant of solute ($J^{1/2}\ m^{-3/2}$ or $MPa^{1/2}$)

v	= Molar volume (m^3 mol^{-1} or dm^3 mol^{-1})
v_1	= Molar volume of supercritical fluid (m^3 mol^{-1} or dm^3 mol^{-1})
v_2	= Molar volume of solute (m^3 mol^{-1} or dm^3 mol^{-1})
z	= Compressibility factor
z^o	= Compressibility factor at standard state
z^r	= Compressibility factor of reference fluid
ω	= Acentric factor
ω^r	= Acentric factor of reference fluid
N	= Total number of data
A, B, C, D, E, F	= Adjustable parameter
W_1	= Mass of carbon dioxide (g)
W_2	= Mass of trapped solute (g)
M_1	= Molecular weight of solvent (g/mol)
M_2	= Molecular weight of solute (g/mol)
AARD	= Average absolute relative deviation (%)
Y^{model}	= y-axis value predicted from model
Y^{exp}	= y-axis value calculated from experimental data
R^2	= Coefficient of determination
SS_{res}	= Residual sum of squares
SS_{tot}	= Total sum of squares
y_i	= Value of y from data set
f_i	= Model value
$\bar{y}$	= Mean of data

CHAPTER 1

INTRODUCTION

1.1 Background

Fluids become subcritical when their pressure and temperature were brought to a region near critical value while they become supercritical when they are heated beyond the critical temperature and compressed beyond the critical pressure. In this state, they have liquid like density and gas like diffusivity (Garlapati & Madras, 2008), which is a good solvent with very unique property that provides quick equilibration and micro pore permeation of the fluid. Due to this exclusive feature, it has been exploited in production of controlled drug delivery systems, pollution prevention and remediation, powder processing, crystallization, bioseparations, methods for spray paint and coatings, polymerization, food processing, chemical reactions, cleaning of semiconductors and precision machinery, dyeing and dry cleaning of textiles, metal de-binding and extractions (Gupta & Shim, 2007).

Occurrence of supercritical phase was first reported by Baron Charles Cagniard de la Tour (1822). From his early experiment, critical point of a substance was first discovered when he observed gas-liquid boundary disappear during heating in a closed glass container. Then, Hannay and Hogarth (1879) first demonstrated the solvating power of supercritical ethanol for cobalt (II) chloride, iron (III) chloride, potassium bromide and potassium iodide while Buchner (Buchner, 1906) reported solubility of some non-volatile organic materials in supercritical carbon dioxide. They have proven solvating power of supercritical fluid is much higher than the value solid vapour pressure could predict.

The dissolving capacity of supercritical fluid hence starts to receive interest at the first half of the twentieth century in process operations. In 1936, Wilson, Keith and Haylett invented a propane deasphalting process for refining lubricating oils by changing solvent power of liquid with changes of temperature and pressure in subcritical point region (Wilson *et al.*, 1936). In 1970s, subcritical pentane was used to remove lower boiling point products from heavier asphaltenes in residuum oil supercritical extraction (ROSE) process by Kerr McGee Corporation (Knox, 2005).

A significant development of supercritical fluid technology can be seen in Zosel's patent in 1971 with extraction of caffeine from green coffee with carbon dioxide (Zosel, 1971). Since 1980, supercritical fluid extraction begins to have rapid development such as extraction of hop (Hubert & Vitzthum, 1978), cholesterol from butter (Mohamed *et al.*, 1998), fragrance and flavour from natural product (Naik *et al.*, 1989), residual solvents and monomers from polymers (Sato *et al.*, 1998) and unsaturated fatty acid from fish oil (Nilsson *et al.*, 1989).

1.2 Problem statement

One of the current issues faced by industrial sector is the lack of clean processes that can produce premium product with low cost. In many pharmaceutical and food industries, organic solvent is still widely used in extraction and particle formation processes. Problems with organic solvents are the flexibility of recycling, contamination of solvent residue in the extract or final product, high cost and environmental pressure (Grodowska & Parczewski, 2010; Beckman, 2004). Compared to organic solvent, supercritical carbon dioxide offers numerous benefits to process yield, environmental aspect, process efficiency, operating cost and time saving, and safety condition. In terms of process yield and efficiency, carbon dioxide is available in high purity which decreases the impurities in product form, while supercritical fluid technology has higher selectivity and lower mass transfer resistance compared to conventional process, which ease the process progression and result in time saving. In order to develop an application using supercritical fluid technology, the fundamental thermophysical properties and phase equilibrium knowledge are important because they can be used to design, scale up and optimize the processes. However, this fundamental knowledge is still limited currently.

Number of research works done on supercritical fluid is abundant but research on subcritical fluid is still not very common, especially subcritical carbon dioxide. Subcritical fluid has temperature between boiling point and critical point and pressure high enough to maintain the liquid state (King & Grabiel, 2007). As temperature rises in subcritical fluid, there is a remarkably decrease of permittivity, increase of diffusion rate and decrease of viscosity and surface tension (Smith, 2006). Consequently, subcritical fluid offers numerous advantages as like supercritical fluid but at lower pressure which is rather inoffensive. Changes of subcritical fluid density with little variation of temperature and pressure are intense in subcritical condition. Thus, it is interesting to know the solubility behavior of solute in subcritical fluid; however this information is very scarce. Therefore, in this work, solubility behavior study in subcritical carbon dioxide was covered to have comparison between supercritical and subcritical in the aspect of solubility trend. This knowledge may be useful in future to replace supercritical fluid with subcritical fluid for milder working conditions.

In order to generalize the solubility behavior of a specific compound, mathematical modeling is needed to estimate solubility data at condition other than experimental one. Mathematical modeling is important because it is time and cost saving to determine solubility behavior of solute at condition that experimental data is not available. Although there are many options of model used for correlation, mathematical modeling is solute dependent and no one universal model can be used to fit all types of solute. In existing solubility study works, not many solubility data was correlated with models. Thus, in this study, some semi-empirical models were tested to fit solubility data in subcritical and supercritical carbon dioxide and detail methodology of employing these models was discussed to simplify the usage of models.

As mentioned, fundamental knowledge of thermophysical properties and phase equilibrium are still limited at present. The solubility data for most pharmaceutical active compounds is either not available or limited to specific thermodynamic range. Caryophyllene oxide and camphene are commonly used as flavor and fragrance agent, still have no available solubility data in subcritical and supercritical carbon dioxide. These two active compounds are from Malaysia local herbs, black pepper (*Piper nigrum* L.) and peacock ginger (*Kaempferia rotunda*). Both of these compounds can be made into essential oils and they have antioxidant effect which can help reduce the toxin effects in the body and promote good health (Kadri *et al.*, 2011; Amiri, 2010). Caryophyllene oxide also has anti-fungal properties which can be used as preservative in food, drugs and cosmetic (Hossain *et al.*, 2008). Of these benefits, solubility behavior of these compounds in supercritical condition is useful to have a cleaner and better process of extraction, separation, purification and synthesis in near future. Thus, this study focuses solubility behavior of camphene and caryophyllene oxide in subcritical and supercritical carbon dioxide for its medicinal values and benefits of subcritical and supercritical fluids.

1.3 Objective

The objectives of this study are:

i. To design and develop an experimental rig that obtains solubility data of interest compound in subcritical and supercritical carbon dioxide.

ii. To investigate the variation of temperature and pressure on the solubility behavior of selected compounds in subcritical and supercritical carbon dioxide.

iii. To identify suitable mathematical correlation that fits and explains the effect of temperature and pressure on the solubility data.

1.4 Thesis outline

The thesis starts with Chapter 1 which outlines the background of research and problem statement in which its significance is established. The scope of research and objectives are discussed in this chapter as well.

Chapter 2 presents the literature review of subcritical and supercritical fluid behavior, their advantages of applying in industrial processes, some common applications of subcritical and supercritical fluid technology such as extraction in food sector, decomposition of waste in environmental management, particle formation in pharmaceutical sector, chromatography, cleaning and particle removal. Mechanism

of solubility measurement, mathematical correlation for solubility data, and solute chosen for the study are critically reviewed as well.

Chapter 3 covers the design of solubility study rig based on the dynamic mechanism. The solubility rig contains an equilibrium cell which solubilizes solid solute into the carbon dioxide in complete saturated phase at desired thermodynamic condition before discharging to collection unit. Method of study, materials used in the experiment, design and development of experimental apparatus, procedure to operate the rig, safety precautions and methodology of correlation by mathematical models are outlined in Chapter 3.

As the rig is designed, validation is compulsory to justify the accuracy and workability of the rig. In Chapter 4, validation results, solubility behavior of camphene and caryophyllene oxide in subcritical and supercritical carbon dioxide, and mathematical models used are discussed.

The thesis ends with Chapter 5 which covers the conclusions and recommendations for future research.

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LIST OF PUBLICATIONS

Yeoh, H.S., Chong, G.H., Mohd Azahan, N., Abdul Rahman, R., Choong, T.S.Y. *A review on solubility measurement in supercritical condition*. Proceedings of the International Conference on Agricultural and Food Engineering for Life (CAFEi) in conjuction with the Malaysia Agriculture, Horticulture and Agrotourism Exhibition (MAHA), Putrajaya, Malaysia, November 26-28, 2012.

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